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NEUTRON SCATTERING OF HEAVY FOSSIL MATERIALS*

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LASER DESORPTION MASS SPECTROMETRY AND SMALL ANGLE NEUTRON SCATTERING OF HEAVY FOSSIL MATERIALS

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INTRODUCTION

The determination of the structural building blocks and the molecular weight range of heavy hydrocarbon materials is of crucial importance in research on their reactivity and for their processing. The chemically and physically heterogeneous nature of heavy hydrocarbon materials, such as coals, heavy petroleum fractions, and residues, dictates that their structure and reactivity patterns be complicated. The problem is further complicated by the fact that the molecular structure and molecular weight distribution of these materials is not dependent on a single molecule, but on a complex mixture of molecules which vary among coals and heavy petroleum samples. Laser Desorption mass spectrometry (LDMS) is emerging as a technique for molecular weight determination having found widespread use in biological polymer research, but is still a relatively new technique in the fossil fuel area. Small angle neutron scattering (SANS) provides information on the size and shape of heavy fossil materials. SANS offers the advantages of high penetration power even in thick cells at high temperatures and high contrast for hydrocarbon systems dispersed in deuterated solvents. LDMS coupled with time of flight has the advantages of high sensitivity and transmission and high mass range. We have used LDMS to examine various heavy fossil-derived materials including: long chain hydrocarbons, asphaltenes from petroleum vacuum resids, and coals. This paper describes the application of laser desorption and small angle neutron scattering techniques to the analysis of components in coals, petroleum resids and unsaturated polymers.

EXPERIMENTAL

The coals used in this study are the Argonne Premium Coal Samples. The procedures for the pyridine extract of the Argonne Premium Coals have been reported previously. The laser desorption mass spectra were recorded on a linear time-of-flight mass spectrometer constructed at Argonne and a Kratos Kompact MALDI III linear/reflectron time-of-flight mass spectrometer. The spectra were produced by exposing the samples distributed as thin layer on a stainless steel sample holder to laser pulses a nitrogen laser. The laser is operated close to the ionization threshold to minimize possible fragmentation of the desorbing material and to optimize resolution. The polyethylene sample were purchased from Petrolite.

Pentane soluble, heptane precipitated asphaltenes and the deasphalted oil (DAO) from vacuum resids of Maya crude oil were obtained from Amoco. The d₁₀-1-methylnaphthalene (d₁₀-1MN) was obtained from Aldrich. Five wt.% dry asphaltene was dissolved in d₁₀-1MN and the solution was stirred overnight. Small angle neutron scattering was performed by placing the sample cell in a boron nitride furnace tube in the small angle diffractometer (SAD) at the Intense Pulsed Neutron Source (IPNS) at Argonne National Laboratory. The temperature of the furnace was measured using a type K thermocouple and maintained within 0.5°C using a Micricon controller. The SAD instrument uses neutrons produced in pulses by spallation due to the deposition of 450 MeV protons on a depleted uranium target, followed by a solid methane moderator (22 K) yielding a wavelength range of 1 to 14Å. Detection of scattered neutrons was accomplished with a 128 x 128 array, 40X40 cm² area sensitive, gas-filled proportional counter, and the wavelength of the scattered neutrons was determined by their times-of-flight. Data were corrected for unit transmission of the sample, the scattering from the stainless steel cell, and incoherent scattering. The accessible q range ($q = 4\pi\sin(q)/l$ where l is the wavelength of the probing neutrons and q is half the scattering angle) using SAD is from 0.008 to 0.2 Å⁻¹.

RESULTS AND DISCUSSION

The mechanisms at work in laser desorption of ions from surfaces is a subject of much speculation and conjecture. Despite the complexity of the ionization mechanism, the facts remain that mass spectra of a large number of volatile organic compounds can be generated by laser desorption at threshold powers and that fragmentation of the parent molecule is minimal at best. Higher laser fluences may alter the ionization process to result in destructive fragmentation, in structurally significant fragmentation, or even ion-molecule reactions. In addition, the desorption event may cause 'clustering' of molecules leading to misinterpretations of the data, i.e., incorrectly assuming that larger molecules are present.

Figure 1 presents the laser desorption mass spectrum of a polyethylene sample of 1000 molecular weight. A silver nitrate matrix is used to produce LD mass spectra of polyethylene by cationization. Each ion is an adduct of silver.

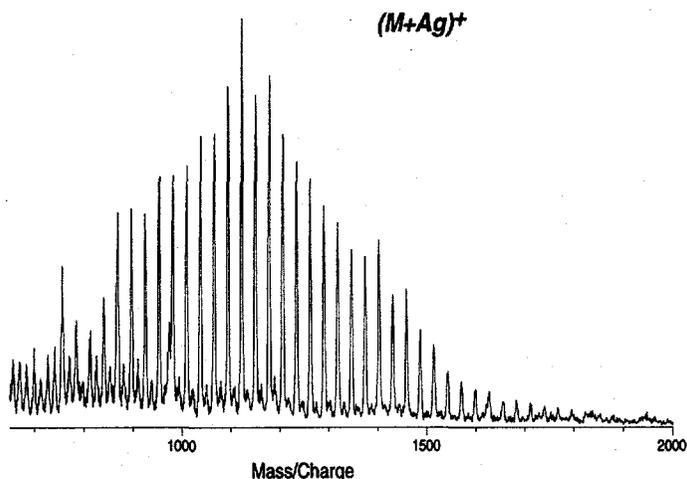


Figure 1. The LDMS spectrum of polyethylene 1000. The ions are produced by cationization with Ag.

Polymer statistics can be calculated from the data. The repeat unit of the polymer can be directly calculated from the mass difference of the oligomer units, and the end groups can also be ascertained. The integrated peak areas (N_i) are used with oligomer molecular weights (M_i) to calculate the number average (M_n) and weight average (M_w) as follows:

$$\begin{aligned}M_n &= N_i M_i / N_i \\M_w &= N_i M_i^2 / N_i \\ \text{polydispersity} &= M_w / M_n\end{aligned}$$

For the polyethylene polymer the number average is 1006 and the weight average is 1045 with a polydispersity of 1.04. To be sure there are some difficulties in these analyses. The lack of polar sites on this compound makes ionization difficult, as ionization in LD generally depends on either low ionization potential with adsorption of the compound (an example is aromatic compounds) or availability of a polar group to which either proton attachment or cationization can occur. One of the practical difficulties of integrating spectra of polymer distribution is knowing where to draw a representative baseline. Very polydisperse systems tend to be problematic.

Coal extracts are readily amenable to LD. Figure 2 shows the LDMS spectra of a homologous ion series found in the pyridine extract of Wyodak coal (APCS 2). One of the strengths of direct LD is that aromatic components are easily ionized and detected.

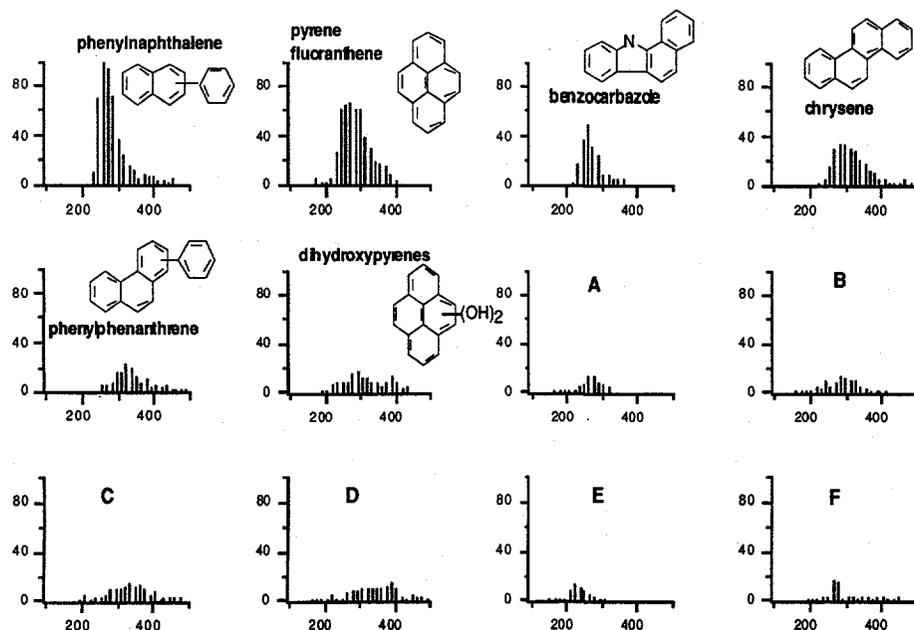


Figure 2. LDMS spectra of the homologous ion series in the pyridine extract of Wyodak-Anderson subbituminous coal (APCS 2)

An interesting result is the four ring systems found in the subbituminous coal. Other ion series, at lower intensities, that have yet to be completely identified (labeled as A, B, C, etc.) show strong evidence for five and six ring systems.

As LDMS is known to chiefly access the aromatic content of a sample, the LDMS of Maya petroleum resid asphaltenes show intense mass spectra like the coal extracts because of their strong aromatic content. The asphaltenes, however, show a higher average molecular weight and a broader molecular weight distribution. The asphaltene has ion intensity extending from a m/z range of ca. 200 to ca. 750. The mass distribution tails to 1000 with exponentially decreasing intensity. Very large molecular species (>1500) are not observed in the asphaltene. The number average molecular weight is quite low, on the order of 500, while the weight average molecular weight, which is more sensitive to the extent of the mass distribution, is on the order of 750. The sample can be considered as a very polydisperse system, at least to first order. Thus, drawing a base line for the high mass region is difficult at best so an upper bound on mass is not possible. However, the bulk of sample has a fairly low molecular weight (about 500 amu).

Gel permeation chromatography and vapor phase osmometry experiments on the asphaltenes indicate that they are rather large structures. GPC shows two size distributions for asphaltenes at approximately 225 and 80 Å. Such structures should have molecular weight very much higher than those found by mass spectrometry. We have, thus, turned to small angle neutron scattering (SANS) to determine the size and shapes of the asphaltenes in solution. SANS was used to investigate the structural changes of a 5 wt.% asphaltene solution in perdeuterated 1-methylnaphthalene (d-1MN) as a function of temperature. A special stainless steel cell was constructed and used for the measurements. The SANS data measured at various temperatures from 20°C to 400°C show that the scattering intensity continuously decreases with increasing temperature. A nonlinear curve in the Guinier plot for asphaltene solutions at 20°C suggested polydispersity in the sizes. Maximum entropy analysis using the form factor for a cylinder allowed extraction of particle size distributions in the radius and length space.

At 20°C the asphaltenes self-associate in d-1MN forming long rod-shaped particles whose radius was around 18Å, but vary in length over 500Å. At 50°C these aggregates break down, as evidenced by the decrease in signal intensity.

In the temperature range of 100 - 320°C the maximum length of the particles decreases and the polydispersity varies in both radius and length dimensions. Between 340 and 400°C, the particles become smaller having a spherical shape with a radius around 12Å.

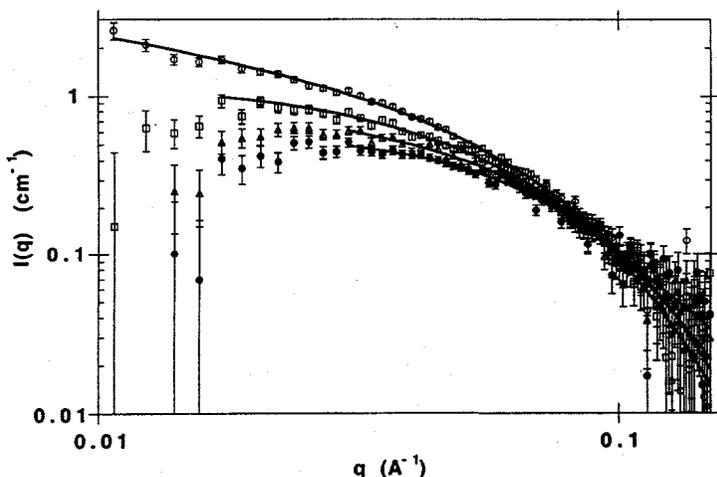


Figure 3: Maximum entropy fits of the SANS data for 5 wt.% asphaltenes in d-1MN at 20°C (o), 50°C (square), 150°C (triangle) and 400°C (filled o).

Upon returning the sample to 20°C, the SANS signal was too weak to derive any structural information, implying irreversible thermochemistry. Interestingly, the structural properties of asphaltenes in d-1MN at temperatures below irreversibility are remarkably reproducible, irrespective of the temperature sequence steps.

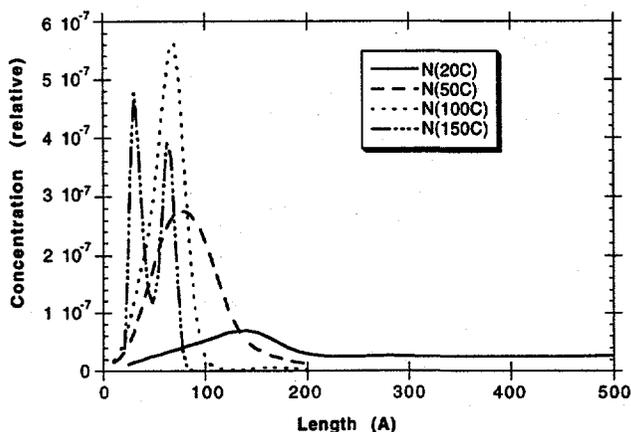


Figure 4: The length distributions for the asphaltene solutions in d-1MN: 20°C (solid line), 50°C(dashed line), 100°C (dotted line), 150°C (dashed-dotted line). The radius is approximately 20 Å for all samples.

Figure 3 shows that maximum entropy analysis is very effective in obtaining the morphology and polydispersity information of the asphaltenes. Figure 4 shows the length distribution for particles of a given radius at 4 different temperatures. The mass spectrometric data and SANS data show that asphaltenes are indeed composed of chiefly low molecular weight molecules (perhaps as low as 500 amu) and that at ambient temperatures aggregate strongly.

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